

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/18472 A2

- (51) International Patent Classification⁷: C08G 63/00
- (21) International Application Number: PCT/US01/26579
- (22) International Filing Date: 24 August 2001 (24.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/228,491 28 August 2000 (28.08.2000) US
- (71) Applicant (*for all designated States except US*): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48674 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): WIEGNER, Jens-Peter [DE/DE]; Mendelejewstrasse 3, 06130 Halle (DE). VOERCKEL, Volkmar [DE/DE]; Weisse Mauer 22, 06217 Merseburg (DE). MUNJAL, Sarat [US/US]; 106 Thyme Trail, Lake Jackson, TX 77566 (US).
- (74) Agent: SIMS, Norman, L.; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 02/18472 A2

(54) Title: PROCEDURE FOR THE MANUFACTURE OF POLY-(ETHYLENE TEREPHTHALATE)

(57) Abstract: The invention concerns a new procedure for the manufacture of poly-(ethylene terephthalate) (PET) by raising the molecular in the liquid phase to 68,000 to 86,000 g/mol, during the step of liquid phase polycondensation and subsequently pelletizing the amorphous product, followed by a crystallization over a period of 15-60 min, at temperatures of 160-185 °C, in air, whereby the pellet temperature reach 25-180 °C. In a subsequent procedural step the pellets remain for 2-10 h at temperatures of 120 °C to 220 °C ("preheater") in an air stream, followed by treating the polyester resin thus obtained with polyols or other blocking agents at concentrations of 100 and 10,000 ppm, relative to the polyester resin.

PROCEDURE FOR THE MANUFACTURE OF POLY-(ETHYLENE
TEREPHTHALATE)

The invention concerns a new procedure for the manufacture of poly-(ethylene
5 terephthalate) (PET).

Poly-(ethylene terephthalate) is a polyester with outstanding application-related
properties that make its use in ever new areas possible. Thus, today PET is not only one of
the most important synthetic fibers, but keeps gaining in importance as a plastic with a
multiplicity of possible uses, such as in the manufacture of bottles and packaging material
10 for food.

The starting products for the manufacture of PET are ethylene glycol and –
depending on the procedure – either dimethyl terephthalate (DMT) or pure terephthalic acid
(PTA).

In the classical DMT process the dimethyl terephthalate is reacted with ethylene
15 glycol in the presence of suitable catalysts (magnesium, calcium or zinc acetate), at
temperatures of 220-260°C, eliminating methanol, to bis-(hydroxyethyl) terephthalate. This
intermediate product is then polycondensed in a vacuum, at temperatures of 260-290°C, in
the presence of suitable catalysts, preferably antimony acetate or trioxide.

With the PTA process, a modern process based on terephthalic acid becomes
20 available. This is made possible by access to highly pure terephthalic acid. In the PTA
procedure, terephthalic acid (PTA) is reacted with ethylene glycol at temperatures of 220-
260°C, under pressure and eliminating water. In this procedure, the terephthalic acid itself
acts as catalyst. In analogy to the DMT procedure, the bis-(hydroxyethyl) terephthalate
formed under these conditions is subsequently polycondensed in the liquid phase, in the
25 presence of suitable catalysts, at temperatures of 260-290°C, under a vacuum. After this
reaction step, the polyester has a mean molecular weight of 30,000 to 65,000 g/mol and an
acetaldehyde content of approx. 30-60 ppm.

Especially high requirements of purity and product properties apply to the use of the
polyester as packaging material. For this reason, in a current procedure the
30 polycondensation in liquid phase is followed by pelletizing of the amorphous polyester, a
crystallization over a period of 5-30 min at temperatures of 160-180°C (pellet temperatures:
25-170 °C) in air, a second crystallization in air over a period of 10-40 min at 165-185°C
(pellet temperatures: 150-180 °C) and an additional procedural step, in which the pellets are

taken to the temperatures of 195-220°C over a period of two to five hours, necessary for the so-called solid state polymerization (SSP) (pellet temperatures: 180-210°C) ("preheater"). The subsequent polycondensation is carried out at temperatures of 195-215°C over a period of 8-20 hours, under nitrogen flow. The molecular weight of the polyester further increases
5 during this procedural step (to approx. 68,000-86,000 g/mol). Easily volatile impurities, such as for instance acetaldehyde, are removed without vinyl esters being able to form anew at these relatively low temperatures, as precursors of acetaldehyde. The acetaldehyde content of the polyester after SSP should lie near approx. 0.1-1 ppm.

Because of the reaction time and temperature and the necessary use of nitrogen, the
10 SSP procedure is especially cost-intensive.

A procedure developed by DuPont in recent years (US 5,599,900) exhibits some general differences. The first reaction stage (esterification) is similar to the conventional procedure. The only difference is the slightly increased temperature during esterification.

Polycondensation in the liquid phase is performed under a nitrogen flow, at
15 temperatures of approximately 250 °C. The use of vacuum technology is thus avoided in this procedural step. This polycondensation step leads to a molecular weight of approx. 12,000-15,000 g/mol. Since in comparison to the molecular weight of 30,000-65,000 g/mol attained in a traditional procedure, this product is considerably less viscous and can hence no longer be pelletized, polycondensation is followed by a procedural step in which pellets
20 are formed from the liquid polyester at temperatures of 240-270°C ("pellet former"). The cooled product is next crystallized under nitrogen at temperatures of 110-190 °C. This is followed by polycondensation in solid phase, over a period of 8-24 hours, at temperatures of 200-240°C, under nitrogen.

The invention is based on the task of finding a simplified procedure for the
25 manufacture of poly-(ethylene terephthalate) that has no deleterious effects on the purity and the characteristic properties of the polyester.

It was surprisingly found that poly-(ethylene terephthalate) can be manufactured with a quality of bottles and sheets suitable for contact with food by foregoing the cost-intensive solid state polymerization, by means of a simple change in the procedure. The new
30 procedure is characterized by an increase in molecular weight during polycondensation in liquid phase, to 68,000-86,000 g/mol. The amorphous product is then pelletized.

This is followed by crystallization over a period of 15-60 min at temperatures of 160-185°C (pellet temperatures: 25-180°C) in air and an additional procedural step, in which the pellets remain in an air flow for 2-10 h, preferably 4-8 h, at temperatures of 120-220°C, preferably 120-190°C ("preheater").

5 In the next procedural step the polyester resin is treated with polyols, in particular sugar alcohols. The addition of these compounds reduces the acetaldehyde content formed during the processing of the polyester. Between 100 and 2,000 ppm sugar alcohol are capable of significantly reducing the acetaldehyde content of the resins, after spraying with a 5-70 percent aqueous solution of these compounds, by addition of a 0.5-50 percent polyol-
10 containing polyester batch, or by addition of crystalline sugar alcohol directly during processing.

Other blocking agents, such as polyamides, are effective in a concentration range of 100 to 10,000 ppm.

It was surprisingly found that the polyesters manufactured according to this
15 simplified procedure have the same processing-related properties and the same low content in impurities, such as acetaldehyde, as the PET resins manufactured according to the classical SSP process.

Some of the catalysts especially suited for the procedure according to the invention are: antimony acetate, antimony trioxide, antimony glycolate; titanates, for instance tetra-
20 isopropyl titanate; partially hydrolyzed titanium halides; zeolites; coprecipitates consisting for instance of titanium/zirconium oxides; untreated and calcined hydrotalcite-like compounds; catalyst/inhibitor complexes consisting for instance of titanates/phosphorus compounds.

The invention will be elucidated below by means of some implementation examples.

25 The determination of the characteristic product features important for PET resins is described in the section below.

The acetaldehyde generation for PET resins takes place according to the following procedure: the polyester resin was processed on an injection molding machine of type ES 200-50 of the Engel company, equipped with a 30 mm diameter screw and an L/D ratio of
30 20.

The PET pellets sprayed with an aqueous sugar alcohol solution were dried in the known manner and then sent to the feed funnel of the injection molding machine under

nitrogen. The mixture was processed (melting and homogenization) at temperatures between 270°C and 300°C. The melt was then injected under pressure into a cooled mold.

Processing parameters:

Drying

- 5 Instrument: circulating air drying oven UT20, Heraeus Instruments
 Temperature: 120 °C
 Duration: 12 h

Injection molding:

- Machine: ES 200-50, Engel company
10 Cylinder temperatures: 277/277/277/277 °C
 Screw speed: 42 rpm
 Cooling time: 10 sec
 Holding pressure time: 10 sec
 Melt residence time: 2.5 min

- 15 The acetal determination for the resins manufactured in the manner described above
 was performed as follows: the various materials were first milled in the presence of liquid
 nitrogen in a centrifugal mill of the Retsch Co. (ZM 1), with a 1 mm sieve. Approximately
 0.1-0.3 g of the milled material were transferred without delay into a 22 ml sampling bottle
 and sealed with a poly-(tetrafluoro-ethylene) seal. The sampling bottles were thermostatted
20 for 90 min at 150°C in a Head Space Oven (Headspace Autosampler HS-40XL by Perkin
 Elmer) and subsequently analyzed by GC (GC-AutoSystem XL by Perkin Elmer) with an
 external standard.

 The calibration curve was obtained by complete evaporation of aqueous solutions
 with different acetaldehyde contents.

25

The instrument parameters used in the acetaldehyde determinations were:

Headspace Autosampler conditions:

- Oven temperature 150 °C
 Needle temperature 160 °C
30 Transfer temperature 170 °C
 Dwell time 90 min

Gas chromatography conditions:

	Column	1.8 m x 1/8" stainless steel
	Filling	Porapak Q, 80/100 mesh
	Carrier gas	Nitrogen, 30 ml/min
5	Combustible gas	Hydrogen
	Air	synthetic air
	Column temperature	140 °C
	Detector temperatures	220 °C

The molecular weight determination for the synthesized resins was accomplished
10 using the variant described in the paragraph below.

To characterize the PET samples, 200 mg of the milled resin were dissolved in 5 ml
1,1,1,3,3,3-hexafluoro-isopropanol. Once the polyester was completely dissolved, 100 µL of
this solution were filled with chloroform into a 2 ml measuring cylinder. The solution was
filtered and analyzed under the following conditions:

15 Instruments:

SEC instrument with Polymer Laboratories (PL) HPLC pump LC
1120
Injector Spark Holland Basic Marathon
Degasser Degasys DG 1210
20 UV/VIS detector PL LC 1200
Column Oven K5 (Tech Lab)

Conditions:

Separation column: 2 columns with PL Gel Mix B, 10 µm (300 x 7.5
mm)
25 Elutrient: chloroform
Temperature: 35 °C
Detection: 263 nm
Analysis time: 25 min
Injected volume: 50 µL

30 Software:

PL-caliber software

Calibration:

External calibration with polystyrene standards (PL)

Example 1 (comparison example)

The synthesis of the polyester resin was performed in a 1.5 L Juchheim reactor. 4
5 mol terephthalic acid (664 g) and 6.4 mol ethylene glycol (397 g) were preplaced together
with 0.6233 g antimony(III) acetate, 0.003 g phosphoric acid and 0.2 g of a 25 percent
tetramethyl-ammonium hydroxide solution.

The closed reactor was heated to 240 °C. The internal pressure rose to 3 bar in the
course of 60 min. From this point on, the internal pressure was adjusted to 2.5-3 bar by
10 means of a valve. Once the internal pressure did not rise anymore (after a total of approx. 90
min), it was reduced every 7 min by 0.5 bar. After stirring for 10 min under nitrogen, at
normal pressure, polycondensation in the liquid phase was started by applying a vacuum.
The internal pressure was reduced at regular intervals, with the maximum vacuum achieved
after 50 min. The reaction was stopped when the desired molecular weight of the polyester
15 was attained. This point in time was determined by the increase in current consumption of
the stirrer motor. The polyester was drained through the bottom valve, cooled in a water
bath and then pelletized. The characteristic values of this polyester resin were determined by
the methods described.

The mean molecular weight of the polyester resin was near 67,000 g/mol. The
20 product had an acetaldehyde content of 51.2 ppm.

After characterization, the polyester was subjected to drying and crystallization for
30 min in a drying oven. Next the product was treated for 60 min at 170°C in a nitrogen
flow ("Crystallizer").

A temperature increase from 170°C to 220°C simulated the conditions in the
25 "preheater", as used in the conventional procedure. The polyester was next polycondensed
for 6 h at 220°C in a nitrogen stream.

The end product had a molecular weight of 79,000 g/mol and an acetaldehyde
content of 1.9 ppm.

After the acetaldehyde generation by injection molding, the processed polyester
30 contained 18.7 ppm acetaldehyde.

Example 2 (example according to the invention)

In an apparatus and under procedural conditions similar to those in Example 1, a high-molecular PET resin was synthesized by liquid phase polycondensation, with a mean molecular weight of 75,000 g/mol. The product contained 86.4 ppm acetaldehyde.

5 The polyester resin was dried and crystallized as in Example 1. The polyester was then treated for another 5 h in an air stream, at 170 °C.

After this thermal treatment, a molecular weight of 76,000 g/mol and an acetaldehyde content of 4.5 ppm were determined.

10 The product described above was processed by three different variants. One third was subjected untreated to acetaldehyde generation under the conditions described. The acetaldehyde content of this product was near 26.7 ppm.

Another third of the product was sprayed with a 35 percent aqueous D-sorbitol solution and subsequently processed by injection molding. The polyester resin loaded with 500 ppm D-sorbitol only contained 17 ppm acetaldehyde. This value lies below the value
15 for the product manufactured according to the traditional procedure.

The last third of the polyester resin was treated with 1000 ppm D-sorbitol by spraying with a 35 percent solution, prior to injection molding. The acetaldehyde content was of only 13.5 ppm.

20 The examples clearly show that it is possible to forego the very cost-intensive solid state polymerization as a procedural step that uses very long reaction times, relatively high temperatures and high-purity nitrogen, in the manufacture of poly-(ethylene terephthalate), by achieving the necessary high molecular weight of the polyester already during liquid phase polycondensation and by reducing the procedure-determined high acetaldehyde contents by treatment of the pelletized polyester at temperatures of at most 190°C in an air
25 stream, over a period of 2-8 hours, by addition of polyols or other acetaldehyde scavengers such as polyamides, during the processing of the polyester, to values that are below those for the extruded products of poly-(ethylene terephthalate), obtained according to the classical procedure.

30 It is obvious that the necessary very high molecular weights of poly-(ethylene terephthalate) can for instance also be attained by reactive extrusion of low-molecular polyesters with poly-carboxylic acid poly-anhydrides, or poly-epoxides. The treatment of

the extruded products in the manner according to the invention also leads to products of poly-(ethylene terephthalate) with low acetaldehyde content.

WHAT IS CLAIMED IS:

1. Procedure for the manufacture of poly-(ethylene terephthalate),
5 characterized by the molecular weight being raised to 68,000 to 86,000 g/mol, necessary for the application in question, during the step of liquid phase polycondensation, the amorphous product being subsequently pelletized, followed by a crystallization over a period of 15-60 min, at temperatures of 160-185°C in air, whereby the pellet temperatures range from 25 to 180°C, followed by a procedural
10 step in which the pellets remain for 2-10 h at 120°C-220°C ("preheater") in an air stream, with the polyester resin so obtained then being treated with polyols or other blocking agents, in concentrations of 100-10,000 ppm, relative to the polyester resin.
2. Procedure for the manufacture of poly-(ethylene terephthalate) according
15 to claim 1, characterized by the residence time in the preheater being of 4-8 hours.
3. Procedure for the manufacture of poly-(ethylene terephthalate) according to claims 1 through 2, characterized by the polyester resin being treated with polyols in concentrations of 100 and 2,000 ppm, relative to the polyester resin.
20
4. Procedure for the manufacture of poly-(ethylene terephthalate) according to claims 1 through 3, characterized by the treatment of the pellets occurring by spraying with a 5-70 percent aqueous polyol solution, by addition of 0.5-50 percent of a polyol-containing polyester batch, or by addition of a crystalline sugar alcohol.
25
5. Procedure for the manufacture of poly-(ethylene terephthalate) according to claims 1 through 4, characterized by the polyols used being sugar alcohols such as D-sorbitol, mannitol, xylitol.
- 30 6. Procedure for the manufacture of poly-(ethylene terephthalate) according to claim 4, characterized by the treatment of the pellets being accomplished by spraying with a 10-50 percent aqueous polyol solution.

7. Procedure for the manufacture of poly-(ethylene terephthalate) according to claim 4, characterized by the treatment of the pellets being accomplished by the addition of a 1-15 percent polyol-containing polyester batch.
- 5
8. Procedure for the manufacture of poly-(ethylene terephthalate) according to claim 1, characterized by using polyamides as blocking agent.